

Pressure induced variation of the ground state of CeAl₃

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Pressure-induced variations of ²⁷Al NMR spectra of CeAl₃ indicate significant changes in the ground-state characteristics of this prototypical heavy-electron compound. Previously reported magnetic and electronic inhomogeneities at ambient pressure and very low temperatures are removed with external pressures exceeding 1.2 kbar. The spectra and results of corresponding measurements of the NMR spin-lattice relaxation rates indicate a pressure-induced emergence of a simple paramagnetic state involving electrons with moderately enhanced masses and no magnetic order above 65 mK.

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At low temperatures, the specific heat of CeAl₃ is dominated by a contribution that varies linearly with temperature. Likewise, a large Pauli type magnetic susceptibility, $\chi(T \rightarrow 0) = 0.036 \text{ emu mol}^{-1}$, indicates a much enhanced density of electron states at the Fermi energy $D(E_F)$, a feature that is typical for heavy-electron compounds [1]. The ground state of CeAl₃ has been investigated with a large number of experimental techniques. An early indication for inhomogeneities of this ground state was provided by μ SR experiments [2, 3] and this conjecture was later confirmed by ²⁷Al NMR results [4]. Subsequently, based on NMR results, Nakamura et al. claimed a magnetically ordered ground state for CeAl₃ [5], while Wong and Clark, again employing NMR, found no evidence for magnetic ordering [6]. The early results suggesting an inhomogeneous ground state revealed two phases; one of them exhibiting quasi static magnetic correlations, leading to a distribution of local magnetic fields at the Al sites, and a second, paramagnetic phase. The corresponding NMR experiments were made on a powder sample and the role of strain effects due to the powdering of the sample material and thus introducing inhomogeneities that mimic an inhomogeneous ground state, remained unclear. NMR experiments under pressure as those presented here aimed at resolving this issue. Experimental data at pressures up to 15 kbar probing the specific heat and the electrical resistivity are available in the literature [7, 8]. To our knowledge, no experimental investigation probing microscopic aspects of binary CeAl₃ under pressure has been reported so far. Our results reveal that the ground state of CeAl₃ is very sensitive to pressure induced volume changes. In particular we note that the two mentioned phases collapse into one at surprisingly moderate pressures.

The ²⁷Al NMR experiments on CeAl₃ at low temperatures and under pressure were made in a top-loading dilution refrigerator. The CeAl₃ powder sample was the same that was investigated in the previous NMR study [4]. A possible deterioration of the sample was checked by repeating the measurement of the NMR spec-

trum at low temperatures and ambient pressure. No detectable changes of the spectra were observed. For the experiments under pressure, a BeCu piston cylinder type pressure cell with 14 (3.8) mm outer (inner) diameter was used. In the pressure cell, the CeAl₃ sample was embedded in paraffin and surrounded by a small NMR rf-coil with a volume of $\sim 1 \text{ mm}^3$. The pressure was determined by the ⁶³Cu nuclear quadrupole resonance frequency of Cu₂O at $T = 1 \text{ K}$ [9]. The powdered Cu₂O, also embedded in paraffin, was placed in a second rf-coil. The NMR resonant circuit consisted of the inductance in the pressure cell containing the sample and of two capacitors placed outside the pressure cell. The NMR signal was monitored with the standard spin echo method using a home built heterodyne, phase sensitive NMR spectrometer. The ²⁷Al NMR spectra were recorded at a fixed frequency, varying the magnetic field. The magnetic field was calibrated using the ¹H NMR resonance from the protons which are present in the pressure medium [10] and in the paraffin. This approach assures that possible magnetic field changes due to paramagnetic impurities in the pressure cell material can be taken into account. Monitoring the width of the ⁶³Cu signal gave evidence that the applied pressure was indeed hydrostatic. The spectral weight (spin echo intensity) was obtained by integrating the detected spin echo signal in the time domain. The spin-lattice relaxation rate (SLRR) T_1^{-1} was measured on the central NMR line with a pulse sequence made up of a comb of 10 pulses (8 μ s rf pulses, 35 μ s time lag), a variable delay and a spin echo sequence. The main experimental difficulty was to cope with the low measuring frequency of about 1 MHz, resulting in very small signals. This and the long spin-lattice relaxation times at low temperatures provoked measuring times of several days for a single NMR spectrum or a magnetisation recovery curve. In order to minimize undesired effects of external magnetic fields on the ground state of CeAl₃, also at elevated pressures, and possible heating effects, we restricted our measurements to Larmor frequencies of the order of 1 MHz.

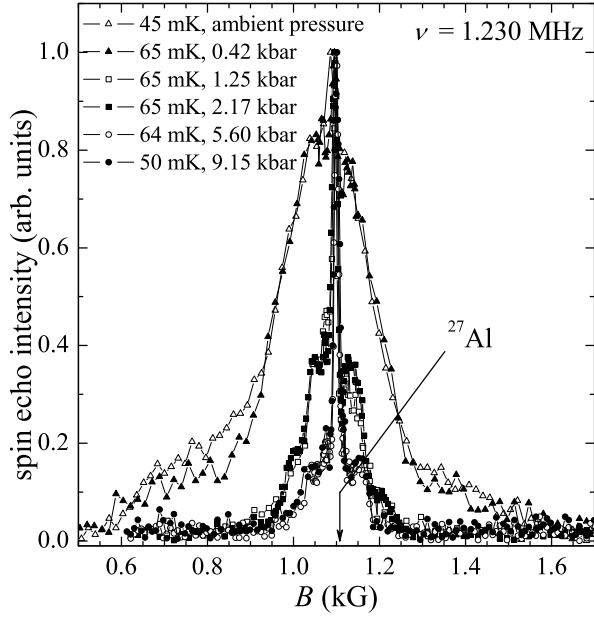


FIG. 1: ^{27}Al NMR spectra of CeAl_3 for different pressures at very low temperatures.

In figure 1, ^{27}Al NMR spectra recorded at $T \approx 65$ mK and at different pressures are displayed. The ambient pressure results coincide with the data obtained in the quoted former work [4] on the same sample. A drastic narrowing of the ^{27}Al NMR spectrum is observed for p exceeding 1.25 kbar. The spectrum then consists of a narrow central line and a broader wing pattern. The spectra recorded at 1.25 and 2.17 kbar are very similar in shape, but still much broader than those obtained at 5.60 or 9.15 kbar. The central line and the wings are both affected by the Knight-shift and the electric-field gradient. Hence, the precise identification of the relevant parameters directly from the spectra is difficult; the employed procedure is explained below. The crystal structure of CeAl_3 has important implications on the ^{27}Al NMR features. The Al sites are on positions with a point symmetry mm in the hexagonal lattice. The low point symmetry dictates axially nonsymmetric tensors and three Al sites must be distinguished. In figure 2, the three different sites are designated as Al^1 , Al^2 , and Al^3 , respectively. The relevant NMR parameters are captured in the tensors for the Knight shift K and the electric field gradient (EFG), respectively. For all three Al sites, the tensors are equal, but rotated by 120 degrees around the c -axis (figure 2). In external magnetic fields with arbitrary orientations, the three Al sites are inequivalent.

In a powder sample all orientations of the crystalline axes with respect to the magnetic field are equally distributed. The calculation of ^{27}Al NMR powder spectra can thus be performed assuming only one Al site as long as no magnetic order or any other symmetry breaking is present. These calculations may be based on an effective

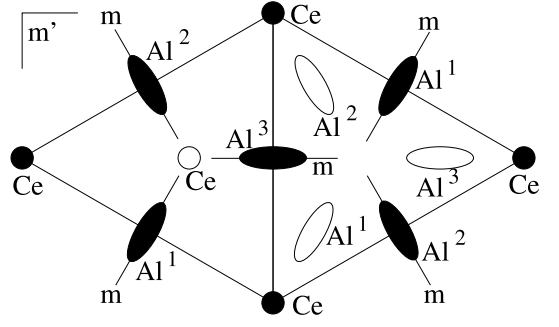


FIG. 2: Symmetry considerations for ^{27}Al NMR in CeAl_3 . The black circles and ellipses denote ion positions, which lie in the same plane perpendicular to the c axis, i.e., the mirror plane m' at $z = 1/4$. The open circles and ellipses are sites at $z = 3/4$

static nuclear Hamiltonian

$$\mathcal{H} = \mathcal{H}_Z(B_0, K_{\text{iso}}, K_{\text{ani}}, \epsilon) + \mathcal{H}_Q(V_{zz}, \eta), \quad (1)$$

i.e., the sum of a Zeeman term \mathcal{H}_Z , including an anisotropic Knight-shift \vec{K} , and a nuclear quadrupolar term \mathcal{H}_Q [11]. The eigenvalues of \mathcal{H} depend on the orientation of the external magnetic field. The largest components of the Knight-shift tensor $K_Z = K_{\text{iso}} + K_{\text{ani}}$ and of the electric-field gradient, V_{zz} , were previously found to be parallel to the c -axis [4]. Thus the spatial relation between the Knight shift and the EFG tensors is known, except for the relative orientation in the $x - y$ plane, which is restricted by symmetry to two cases with either $V_{xx} \parallel K_X$ or $V_{xx} \parallel K_Y$. It is assumed that these symmetry relations are not altered by the application of moderate hydrostatic pressures. With these considerations the powder spectra could fairly well be reproduced by simulation calculations, varying the free parameters given in equation 1 (see figure 3). The non-perturbative calculation was based on a full diagonalisation of the static nuclear Hamiltonian and the powder spectrum was simulated with 10'000 arbitrary crystalline orientations. The parameters, which were found to reproduce the spectra are summarised in table I [12]. Our extensive simulations, involving a wide range of parameters, allowed the estimate of statistical uncertainties shown in table I. These uncertainties represent the change of the parameters that would increase chi-squared by 50%. The change in K_{iso} is thus significant, because it varies by a factor 2 over the covered pressure range.

In the experiments probing the SLRR at non zero pressure, we irradiated only the narrow central line in a field range of approximately ± 30 G around the maximum [13]. Therefore, the recovery of the nuclear magnetisation cannot be described by a single exponential and the data need to be fitted to the relevant multiexponential func-

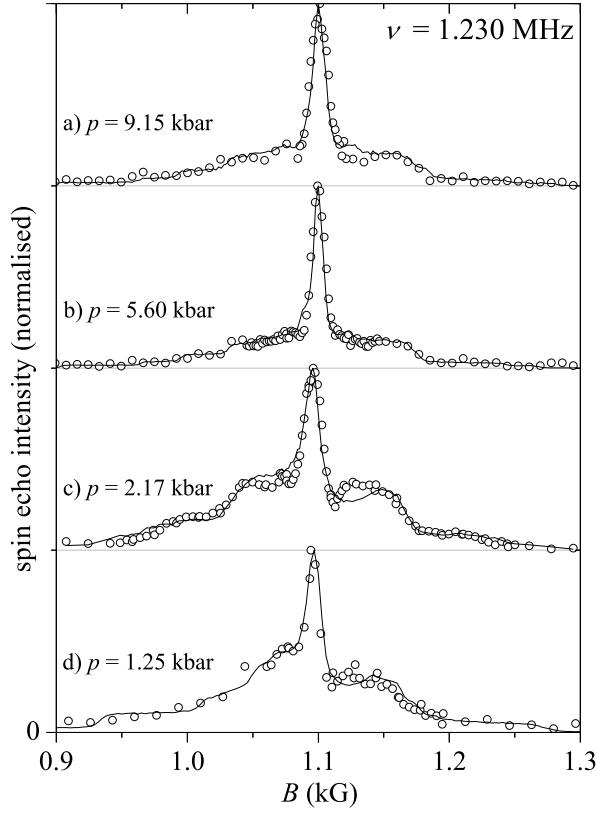


FIG. 3: Simulated ^{27}Al NMR spectra (solid lines) of CeAl_3 for different pressures. Empty circles represent the same experimental data as in figure 1.

| p (kbar) | K_{iso} (%) | K_{ani} (%) | ϵ 1 | V_{zz} (a.u.) | η 1 | LW (kHz) |
|---------------|-------------------------|-------------------------|-----------------|--------------------|-------------|---------------|
| 1.25 | 2.1(2) | 3.5(9) | 0 | 0.026(3) | 0.40(10) | 4 |
| 2.17 | 2.1(2) | 3.2(8) | 0 | 0.026(3) | 0.15(4) | 6 |
| 5.60 | 1.0(1) | 1.0(3) | 0 | 0.018(2) | 0.50(13) | 2 |
| 9.15 | 0.9(1) | 0.8(2) | 0 | 0.021(2) | 0.45(11) | 3 |
| ambient | 2.1(1) | 0.8(1) | 0 | 0.019 | 0.2 | - |

TABLE I: Summary of the parameters used for the calculated ^{27}Al NMR spectra. K_{iso} , K_{ani} and ϵ represent the anisotropic Knight-shift, V_{zz} and η characterise the electric-field gradient. The parameter LW reflects the broadening of the calculated discrete resonance-fields. The last row cites data from [14], evaluated at 35 mK, for comparison. Numbers in parenthesis are error estimates of the respective parameters.

tion [15]

$$1 - \frac{m(t)}{m(\infty)} = \frac{9}{35}e\left(-\frac{t}{T_1}\right) + \frac{4}{15}e\left(-\frac{6t}{T_1}\right) + \frac{10}{21}e\left(-\frac{15t}{T_1}\right). \quad (2)$$

As explained in [4], the spin-lattice relaxation is rather complicated at ambient pressure (and also at 0.4 kbar). Here we restrict ourselves to pressures at and above 1.25 kbar, where the “correlated phase” is suppressed (see fig. 1). The fraction of powder grains, where the

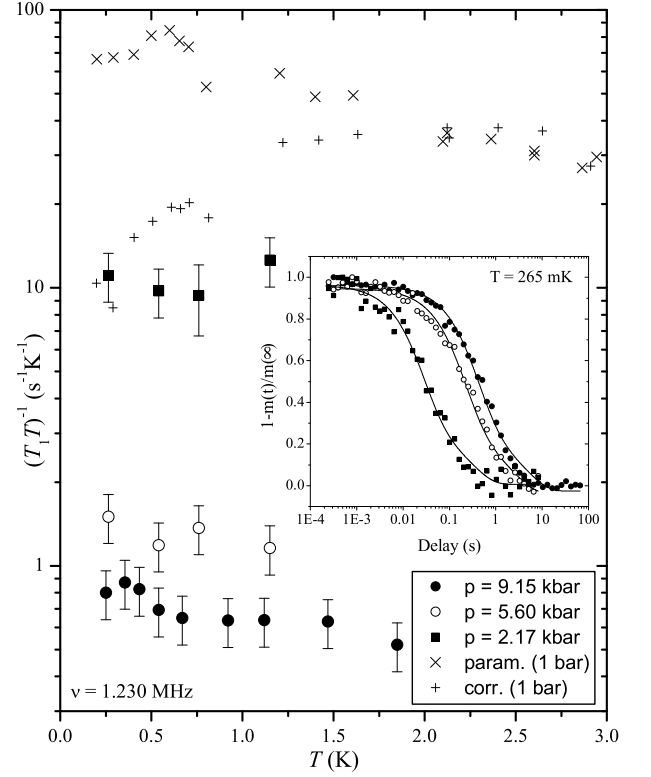


FIG. 4: ^{27}Al SLRR of CeAl_3 for different pressures and temperatures. We also measured T_1 at 1.25 kbar at the lowest temperature. The corresponding value is very close to that measured at 2.17 kbar. Ambient pressure data are taken from [4]. For LaAl_3 , the T -independent value for $(T_1T)^{-1} = 0.037 \text{ (sK)}^{-1}$ [16].

quadrupolar signal is within the irradiation window, is less than 15%. This leads to a correction of the above recovery function and to the values of T_1 , in the form of a reduction of maximally 20%. In figure 4, the low temperature relaxation rates T_1^{-1} divided by the temperature T are plotted versus T for various pressures. Shown for comparison are the ambient pressure data that were reported in ref. [4]. The ‘ \times ’ symbols are relaxation rates from the spectral part between 0.9 and 1.3 kG, reflecting the paramagnetic phase and the ‘+’ symbols represent data points obtained from the broadest part of the ambient pressure spectrum (see figure 4). Most obvious is the significant reduction of $(T_1T)^{-1}$ with increasing pressure by almost 2 orders of magnitude in the covered pressure range. This signals a diminishing density of electronic states at the Fermi energy and is in qualitative agreement with the pressure induced reduction of the Knight shift components that results from the analysis of the ^{27}Al NMR spectra. The temperature variation of $(T_1T)^{-1}(T)$ is fairly small for non zero pressures. Considering the spectra in fig. 1 and the T_1^{-1} data in fig. 4 it may be noted that the pressure-induced single phase does not order magnetically above 50 mK. This and the reduction

| p | $(T_1 T)^{-1}$ | $T_1 T K_{\text{iso}}^2$ | R |
|------|-------------------------------|--------------------------|-------------------|
| kbar | $\text{s}^{-1} \text{K}^{-1}$ | 10^{-6} s K | 1 |
| 0 | 68 | - | - |
| 2.17 | 10 ± 2 | 44 ± 10 | 0.088 ± 0.021 |
| 5.6 | 1.2 ± 0.24 | 83 ± 20 | 0.046 ± 0.011 |
| 9.15 | 0.7 ± 0.014 | 115 ± 28 | 0.033 ± 0.008 |

TABLE II: Pressure dependence of relaxation-related NMR parameters for the paramagnetic phase at low temperatures.

of $D(E_F)$ are both consistent with previously published specific-heat data obtained at high pressures [7]. In table II we list approximate values of $(T_1 T)^{-1}$, $T_1 T K_{\text{iso}}^2$ and the parameter R which appears in the well known relation [17]

$$T_1 T K^2 R = \frac{\hbar}{4\pi k_B} \left(\frac{\gamma_e}{\gamma_N} \right)^2. \quad (3)$$

The parameter R reflects the ratio between the effective magnetic susceptibility χ and density of electronic states $D(E_F)$. The decrease of R must therefore be traced back to a strong reduction of $\chi(q)$. A previously published neutron scattering study on La-doped CeAl_3 [18] also indicated that pressure diminishes the tendency to a magnetic instability in that material at low temperatures. We emphasize that our main claims do not depend on the results of the details of the analysis. They are evident from the raw data. Nevertheless, also the quoted pressure-induced variations of the relevant parameters resulting from our quantitative analysis are significant.

We conclude that in CeAl_3 the inhomogeneous ground state is quenched by the application of moderate pressures. The so-called correlated phase, reflected in the broad part of the low-pressure Al NMR spectra, vanishes upon increasing external pressure between 0.42 and 1.25 kbar. The remaining phase is modified in the sense that we observe a clear drop in $D(E_F)$ with increasing pressure, reflected in the SLRR and in the Knight shift, which has also been suggested on the basis of macroscopic quantities such as the specific heat or the electrical resistivity [7, 8]. The observations imply that the inhomogeneous ground state at ambient pressure is indeed an intrinsic property of CeAl_3 and that the broad line, previously attributed to the correlated phase, is not simply an artefact. A more detailed account of this work will be published elsewhere.

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